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Studies on Activation Mechanism for Au/Zn CO-Sensing Systems

A recent paper describes the use of Fourier Transform Infrared Spectroscopy (FTIR) and quadruple mass spectroscopy to assist in understanding the processes of adsorption and oxidation of CO on an Au/ZnO sample (1). $^{16}O_2$ and $^{18}O_2$ were used to demonstrate that CO adsorbed on gold sites at the perimeter interface with ZnO reacts with surface lattice oxygens to form carbonate-like intermediates. It is claimed that this reaction and the decomposition of the intermediates is the principal reason for the conductivity changes in the semiconducting metal oxide when in contact with CO in air.

The oxygen adsorbed from the air onto gold vicinal sites facilitates nucleophilic attack by surface oxygen on the CO. It had been previously shown that highly dispersed gold appreciably enhances the sensitivity and selectivity to CO detection (2). The samples for the recent study were prepared by co-precipitation from $HAuCl_4$ and $Zn(NO_3)_2$ solutions, followed by calcination in air at 400°C. TEM micrographs showed that the gold particles were homogeneously dispersed on ZnO, with particle diameters smaller than 5 nm (1, 3). The infrared spectra were run at room temperature in an infrared cell designed to examine samples *in situ*, under controlled atmospheres.

The results showed that:

- CO is activated by gold in three molecular forms: a linear carbonyl species bonded at Au terrace, step and kink sites, a carbonyl species bonded to Au borderline sites, and a carbonyl species also interacting with Zn cations, via the π-orbitals.
- The high CO oxidation activity of Group 11 (IB) elements supported on ZnO can be related to the high basicity of oxygen atoms adsorbed on these metals and/or to a perturbation of the oxide defect equilibria by metal/oxide junction effects.
- Two independent pathways are possible for CO oxidation on the Au/ZnO sample, i.e. molecular oxygen reacts directly with CO at the surface of the gold particles, leading to the formation of molecular CO_2, or molecular oxygen activates or enhances the reactivity of CO species adsorbed at the border of gold particles with the surface oxygens.
- The electron-withdrawing effect of the adsorbed oxygen facilitates the nucleophilic attack of surface oxygens on the CO.

The chemistry described in this paper could be used as a basis for catalytic gas sensor systems designed for the detection of carbon monoxide.

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